Vignette

ELECTRON TRANSFER REACTIONS

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Electron transfer reactions are ubiquitous in chemistry. An example is the transfer of an electron from the reduced form of a reactant A, A (red), to the oxidized form of a reactant B, B (ox), in solution,

$$A \text{ (red)} + B \text{ (ox)} \rightarrow A \text{ (ox)} + B \text{ (red)}. \qquad (1)$$

When one of these reactants B is an electrode M, we have the electrochemical reaction:

$$A \text{ (red)} + M \rightarrow A \text{ (ox)} + M(e). \qquad (2)$$
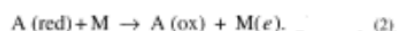
Electron transfers occur for inorganic systems and organic ones, for reactions in solution and for those across interfaces, in complex biological systems and in very simple systems. The field of electron transfer processes has grown exponentially in recent decades and continues its expansion. In this vignette, we would like to describe briefly the principal physical ideas on how an electron transfer occurs, what predictions the theory makes, how those predictions compare with the experimental results, and some uses of the theory (see Marcus).

We consider first the simplest of all electron transfers, a self-exchange reaction, one of the many being

$$MnO_4^= + MnO_4^- \rightarrow MnO_4^- + MnO_4^= \qquad (3)$$

in aqueous solution. Experimentally the rates of such reactions were initially measured, for a wide variety of central metal atoms and of ligands (here, Mn and O, respectively), by labeling one of the metal atoms in a particular valence state with a radioactive atom as a tracer and following its appearance in the other valence state.

The central idea underlying the theory of electron transfer is two-fold and can be illustrated using reaction (3): When the electron jumps from the $MnO_4^=$ to the MnO_4^-, it does so so rapidly that the atoms in the reactants and in the solvent molecules do not have time to move in that brief instant, since the atoms are much heavier than an electron—i.e., the transfer should obey the Franck–Condon principle. This constraint has major consequences. We first recall that the solvent dipolar molecules are partially oriented, on the average, towards the ions, and much more so toward the more highly charged ion. Thus, each of the newly formed ions in reaction (3) suddenly finds itself in a wrong solvent environment. If the electron transfer occurred in this way, the total energy of the system would therefore suddenly increase. However, if such a transfer occurred in the absence of absorption of light, this mechanism would violate the law of energy conservation. Accordingly, for a thermal electron transfer to proceed, an appropriate redistribution of the orientations of the solvent molecules in the vicinity of each ion needs to occur prior to the electron transfer. With a suitable such fluctuation both the Franck–Condon principle and energy conservation can be satisfied simultaneously, whereas the latter would be violated in the absence of this fluctuation.

Formulating an electron transfer theory involved devising a way for finding this needed redistribution, using it to describe the transition state of the reaction and so calculate the reaction rate. Initially, we used a dielectric continuum model for the solvent and set up an expression for the free energy G of such a dielectric continuum undergoing fluctuations ("nonequilibrium dielectric polarization"). This G was obtained by finding a reversible path for forming such a nonequilibrium state of the solvent, with an arbitrary dielectric polarization function $P(r)$ at each point r in the system and calculating the reversible work to form that state. To find the $P(r)$ characterizing the transition state of the reaction, G was minimized subject to the constraint that the transition state was an ensemble of configurations of the system that satisfied the Franck–Condon principle and the energy conservation upon electron transfer.

An expression for the rate constant of the reaction k_{rate} was obtained in this way and can be written as

$$k_{rate} = A e^{-\Delta G^*/k_B T} \qquad (4)$$

$$\Delta G^* = (\lambda / 4)(1 + \Delta G^0 / \lambda)^2, \qquad (5)$$

where ΔG^0 is the standard free energy of reaction (1), λ is a "reorganization energy" that was expressed in terms of properties of the solute (e.g., size, vibrational bond length changes) and of dielectric properties of the solvent. An equation analogous to Eq. 5 was derived for electron transfers at electrodes, with ΔG^0 replaced by the activation overpotential $e\eta_{act}$ of the electrode reaction (2).

Some "work terms" to bring the reactants to a suitable electron transfer distance and to separate the reactant products are omitted for brevity in Eq. 5. The value of A in Eq. 4 depends on the strength of the electronic coupling between the two reactants.

We later show that Eq. 5 is actually more general than the dielectric continuum model on which it was originally based: Using a statistical mechanical description, a special (global) reaction coordinate ΔU was introduced, and a linear response approximation for the solvent medium was then used (e.g., the dielectric polarization is proportional to the electric field). In this case the free energy of a suitable fluctuation becomes a quadratic function of ΔU, leading again to Eq. 5. This ΔU is, for any configuration q of the nuclei of the entire system, the difference of the potential energies $U_p(q)$ and $U_r(q)$ for the entire system, for the products and reactants, respectively.

One of the major initial predictions of the theory stemmed from a very useful additivity property of λ: the λ for a cross-reaction, reaction (1), i.e., an electron transfer between two different redox systems, A and B, is approximately the mean of that for the self-exchange reaction of A and that of B, $\lambda_{12} \cong \frac{1}{2}(\lambda_{11} + \lambda_{22})$. A consequence of this result, in conjunction with Eqs. 4 and 5, is the "cross-relation" between the rate constant k_{12} and the two self-exchange rate constants, k_{11} and k_{22}:

$$k_{12} \cong (k_{11} k_{22} K_{12} f_{12})^{1/2}, \qquad (6)$$

where K_{12} is the equilibrium constant of reaction (1) $[RT \ln K = -\Delta G^0]$ and f_{12} is a known function of the three other quantities in the right-hand side of Eq. 6 and is usually close to unity.

A second prediction from the equations concerns the effect of systematically varying ΔG^0 for a series in which one of the reactants is held constant, but the other is varied, so that λ is approximately constant, frequently achieved by varying a substituent in some aromatic ligand. The prediction was that the dependence of $\ln k_{rate}$ on ΔG^0 is given by Eqs. 4 and 5. For example, the slope of a $\ln k_{rate}$ vs. $\ln K$ plot, where K is the equilibrium constant, was predicted to be 0.5 when $|\Delta G^0|/\lambda$ is small. Curvature was predicted when $|\Delta G^0/\lambda|$ becomes larger. A dramatic prediction that was subsequently widely explored was the "inverted effect": When ΔG^0 is made increasingly negative, the k_{rate} at first increases, according to Eqs. 4 and 5 but then decreases when $-\Delta G^0$ is so large that $|\Delta G^0| > \lambda$.

For an electrode reaction the dependence of the rate constant for electron transfer between the reactant and the

electrode was predicted to obey the quadratic formula, with ΔG^0 replaced by $e\eta_{act}$, until $|e\eta_{act}| \cong \lambda_{el}$, where λ_{el} is the λ for the electrode reaction and then become constant. When $e\eta_{act}$ is not large the Tafel coefficient for the electrochemical reaction step, which expresses how the current for the forward or reverse electron transfer varies with $e\eta_a$, is predicted in this way to be about 0.5 and that the Tafel plot should become curved at large values of $|e\eta_{act}/\lambda|$ and be quadratic up to $|e\eta_{act}| = \lambda$. In another prediction k_{rate} of a self-exchange reaction was related to the corresponding rate constant of the electron exchange reaction of the reactant with the electrode in reaction (2).

Another prediction involves the absolute value of the rate constant. Using the difference in bond lengths of the two redox forms of a reactant (inferred from EXAFS data for ions in solution or from x-ray crystallography, for example), the vibrational force constants (from Raman spectra, for example) and, in the case of the dielectric continuum model, the known dielectric properties of the solvent, the k_{rate} of the self-exchange reactions have been calculated and compared with experiment.

Each of the above predictions has been tested experimentally. The first to be widely tested was the cross-relation, Eq. 6: the k_{11}'s, k_{22}'s, and K_{12} could be determined experimentally, and so k_{12} could be predicted. This equation has been largely confirmed, except for some anomalous cases. Because of this confirmation, Eq. 6 has also been used occasionally to estimate unknown standard electrode potentials from the k's.

The dependence of the rate constant on ΔG^0 (chemical) or $e\eta_a$ (electrochemical) has also been tested and found to be close to 0.5 when those quantities are not large. Self-assembled organic monolayers have been recently used to retard the rate and to reduce slow diffusion as a rate controlling step, or eliminate it by tethering the A in Eq. 2 to the monolayer. Use of these monolayers permitted an accurate curvature of the Tafel plot to be tested and agreement with theory was obtained.

The relation between self-exchange rate constants and the corresponding electrochemical rate constants has also been tested and, except for some very fast reactions, has been approximately confirmed. The expression relating the self-exchange rate constant to the dielectric properties of the solvent has been helpful in showing trends, but sometimes specific solvent effects enter, and require a molecular rather than a continuum treatment. With this reservation, there has also been approximate agreement of the data with the theoretical expression for the absolute reaction rates.

The most unusual prediction of the theory was the "inverted effect." It was the last prediction to be confirmed, and was done so by Miller, Calcaterra, and Closs in 1984 in a now famous experiment about 25 years after the prediction was first made in the literature. Since then there have been many other confirmations of the effect. An earlier indirect confirmation had been obtained for electrochemically generated reactants, for which it was observed that 100% of a reaction of a highly exothermic electron transfer went to form a product in an excited electronic state: The inverted effect had reduced considerably the probability of forming that product in its usual (ground) electronic state. By forming the excited electronic state the effective ΔG^0 for that reaction step was reduced to a small value. The excited states were detected, ultimately, by observation of the luminescence (chemiluminescent reaction).

The breadth of applications of theory are illustrated in the accompanying diagram, Fig. 1. One of the applications
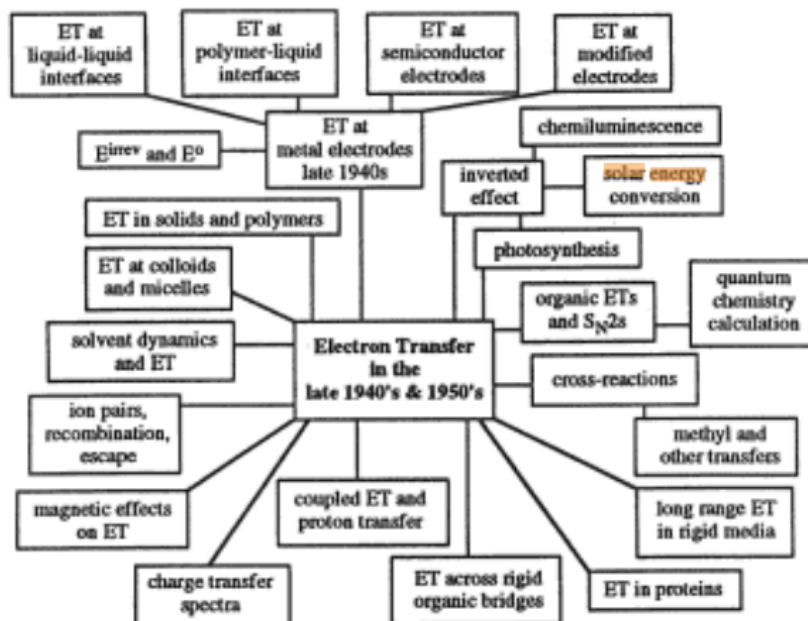

Figure 1 Growth of the electron transfer field.

of the inverted effect, for example, is in solar energy conversion. The efficiency of the photosynthetic reaction system has been attributed, in part, to that effect. The electron transfer theory serves to link the many fields given in the figure and has pointed the way for obtaining new relationships in other areas, such as the testing of the cross-relation for the atom, ion, and group transfer reactions, with good agreement with the experiments.

● REFERENCES

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